In order for the proton transfer steps k_3 and k_4 to be rate determining for pathway B at pH >1, the initial product of uncatalyzed methoxyamine attack, $T^{\pm}$, must revert rapidly to starting materials (with a lifetime of $\sim 10^{-9}$ sec) unless it is trapped by proton transfer.[4] As the pH is decreased, the acid-catalyzed proton transfer to $T^{\pm}$, $k_3 a_{H^+}$, becomes faster than the uncatalyzed attack and expulsion of methoxyamine and the rate for the reaction should eventually level off, with a rate constant equal to k_2, unless another mechanism for the addition reaction becomes available. This additional mechanism is provided by the hydronium ion catalyzed pathway A. The detailed mechanism for this pathway may involve either a proton transfer that is in some sense "concerted" with carbon–nitrogen bond formation, by analogy with the proposed mechanism for semicarbazone,[5] thiosemicarbazone,[6] and methylthiosemicarbazone[7] formation, or an attack of the nucleophile on the fully protonated aldehyde.

The steady-state rate law for the overall reaction is given by eq 2 and 2a, where K_{ad} is the equilibrium constant for formation of the neutral carbinolamine. The apparent rate constant, k_{at}', for carbinolamine formation is the sum of the rate constants for pathways A and B for the addition step described above. Experimentally, k_{at}' is obtained by correction of the observed second-order rate constant at any given pH for the contribution of the dehydration step,[6] $K_{ad}k_5a_{H^+}$. Individual rate constants determined from the dependence on hydrogen ion activity of the observed rate constant for O-methyloxime formation are given in Table I.

$$k_{obsd} = \frac{k_{at}'K_{ad}k_5a_{H^+}}{k_{at}' + K_{ad}k_5a_{H^+}} \tag{2}$$

$$k_{at}' = k_1a_{H^+} + \frac{k_2(k_4 + k_3a_{H^+})}{k_{-2} + k_4 + k_3a_{H^+}} \tag{2a}$$

Table I. Kinetic Constants for O-Methyloxime Formation from p-Chlorobenzaldehyde in Aqueous Solution at 25° [a]

K_{ad} (M^{-1})	13.4 ± 0.6[b]
k_1 (M^{-2} sec^{-1})[c]	2070
k_2 (M^{-1} sec^{-1})	1150
k_3k_2/k_{-2} (M^{-2} sec^{-1})[d]	4.0×10^4
k_4k_2/k_{-2} (M^{-1} sec^{-1})	25 ± 5
$K_{ad}k_5$ (M^{-2} sec^{-1})[d]	2.1×10^5

[a] Rate constants are for the processes defined in eq 1. Ionic strength was 1.0 M (KCl) except at high acid concentrations. [b] S. Rosenberg, unpublished observation. [c] Rate constant based on antilog ($-H_0$) (M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957)), at HCl concentrations ≥ 1.0 M. [d] Based on hydronium ion activity.

The solid line of Figure 1 for p-chlorobenzaldehyde, calculated[8] from these constants, is in good agreement with the experimental points.

Support for the proposed mechanism is provided by calculation of the rate constants k_3 and k_4 from the kinetic data of Table I and an estimated equilibrium constant,[9] k_2/k_{-2}, of 4×10^{-6} M^{-1} for the formation of $T^{\pm}$ from starting materials. The estimated values of $k_3 = 10^{10}$ M^{-1} sec^{-1} and $k_4 = 6 \times 10^6$ sec^{-1} are consistent with the expected rate constants for a thermodynamically favorable diffusion controlled proton transfer[12] and a solvent-mediated "proton switch" of the zwitterionic intermediate,[13] respectively.

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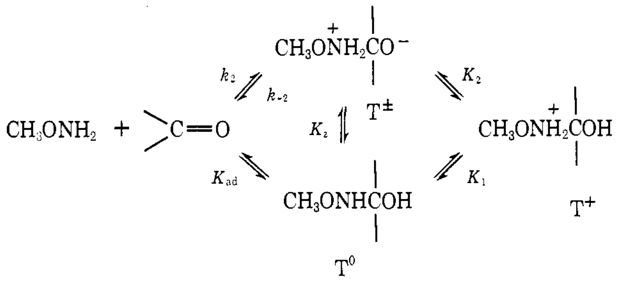
(9) This equilibrium constant is equal to $K_{ad}K_z$, where K_{ad} is the measured equilibrium constant for formation of the neutral carbinolamine and K_z is the equilibrium constant for conversion of T^0 to $T^{\pm}$



A value for K_z of 3×10^{-7} is calculated from values of 2.0 and 8.5 for pK_1 and pK_2, respectively, estimated from pK_a = 4.88 for N,O-dimethylhydroxylammonium ion,[10] pK_a = 10.0 for the hydroxyl group[11] of $CH_3N^+H_2CH_2OH$, and structure–reactivity correlations.[7]

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Photoelectron Spectroscopy and the Anodic Fragmentation of Adamantane Derivatives

Sir:

We wish to report an unusual, new anodic fragmentation reaction of an aliphatic ketone and the first use of photoelectron spectroscopy in understanding electrochemical phenomena.

It has been previously demonstrated[1] that the anodic oxidation of adamantane (**1**) at platinum in acetonitrile produces N-(1-adamantyl)acetamide (**2**). This oxidation involves initial electron transfer from the hydrocarbon to the electrode. The cation radical produced in this reaction then loses a proton and an electron forming the 1-adamantyl cation. This cation is finally converted to amide **2** in analogy with the Ritter reaction.

Anodic oxidations of several adamantane derivatives have now been undertaken and we report here on 1-acetyladamantane (**3**) and 1-carbomethoxyadamantane (**4**). Ester **4** was potentiostatically oxidized at 2.45 V *vs.* Ag|0.1 M $AgNO_3$ in damp acetonitrile. The current decayed from 180 mA down to the background level of 3 mA over a 3-hr period. Work-up by concentration of the anolyte and extraction with ether provided 1-

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(1) V. R. Koch and L. L. Miller, *Tetrahedron Lett.*, 693 (1973).

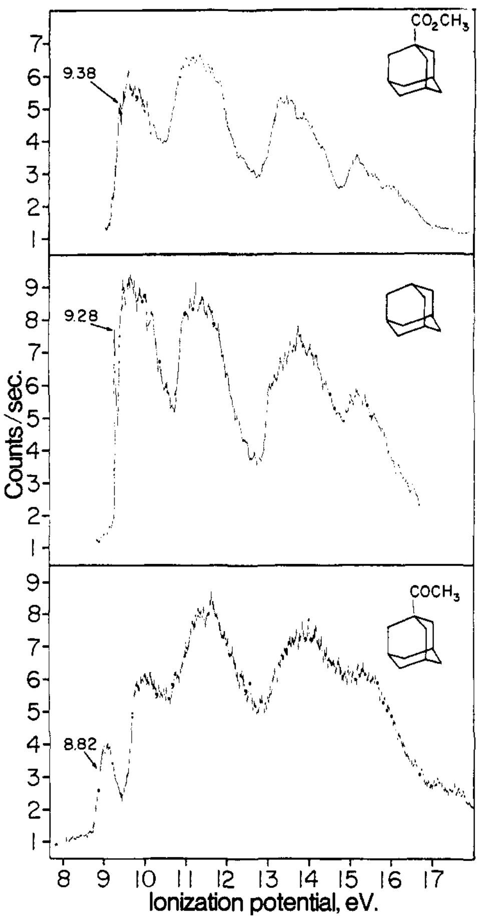
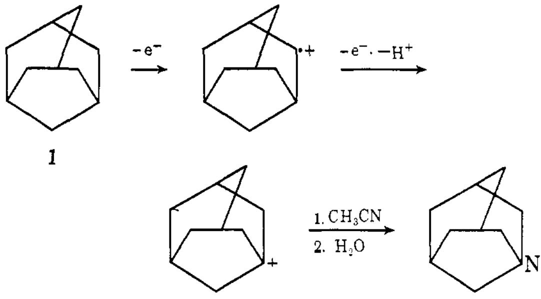
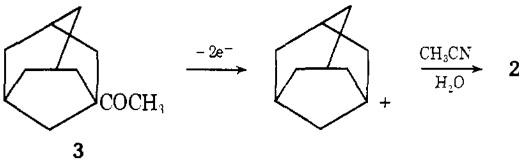


Figure 1. He(I) photoelectron spectra.



acetamido-3-carbomethoxyadamantane in 62% yield. The structure was proven by nmr, mass, and ir spectra and a satisfactory elemental analysis. Thus, the overall reaction is analogous to that of the parent adamantane. Contradistinctively, ketone **3** did not lose a bridgehead



proton, but lead exclusively to amide **2** when it was oxidized at 2.35 V.

This disparity between the chemistry of the two very similar reactants, **3** and **4**, was unexpected, but was resolved through the use of photoelectron spectroscopy. The He(I) photoelectron spectra of **1**, **3**, and **4**, recorded using a Perkin-Elmer Model PS-18 spectrometer, are shown as Figure 1. An important feature of this comparison is the similarity of the position (Table I) and shape of the bands for the first ionization potential of 1-carbomethoxyadamantane (**4**) with **1** and substituted adamantanes.[2-4] In contrast, the first adiabatic ionization potential of the ester, methyl pivalate, is significantly higher (9.90 eV), which reinforces the conclusion that the lowest electronic state available for the cation radical of **4** has the vacancy residing in the adamantyl moiety.

Table I. Oxidation Potentials and Ionization Potentials

Compd	$E_p/2$, V[a]	I.P. adiabatic, eV
4	2.56	9.38 ± 0.03
1	2.36	9.28 ± 0.1[b]
3	1.96	8.82 ± 0.05
Pinacalone	2.18	8.88 ± 0.04
Methyl pivalate	>3.0	9.90 ± 0.04

[a] Sweep rate 0.1 V/sec; Ag|0.1 N AgNO$_3$ reference electrode. [b] Lit.[2] 9.31 ± 0.01.

The situation with 1-acetyladamantane (**3**) is quite different. The first ionization potentials of **3** and pinacolone are virtually the same (Table I), both being significantly lower than that of adamantane. The vibrational spacing in these bands has not been well resolved but the main component has a spacing of ~700 cm^{-1} in both cases. The first photoelectron spectroscopic band in aliphatic aldehydes and ketones is due to the loss of an oxygen lone-pair electron[5] and this applies to the present ketones as well. The difference in ionization potential between ketones and esters is adequately rationalized in terms of inductive effect of the second oxygen atom of the ester.

As shown in Table I, there is a fair correlation between the ionization potentials and $E_p/2$ values from cyclic voltammetry in solution. This is consistent with the hypothesis that the anodic reactions involve initial cation radical formation. The photoelectron spectroscopic data indicate that initial electron transfer from ester **4** should involve the adamantyl moiety and, indeed, the resulting chemistry is confined to this part of the molecule. In contrast, ketone **4** should initially give up an electron from the nonbonding carbonyl oxygen and an α cleavage with analogy in ketone mass spectrometry[6] results.

The use of photoelectron spectroscopy to understand electrochemical reactivities should be an increasingly useful activity as both techniques undergo further development. In addition to defining the gross nature of the ionic states, the vibrational fine structure in the photoelectron spectra may give indications of the type of chemical reactions to be expected from cation radicals.

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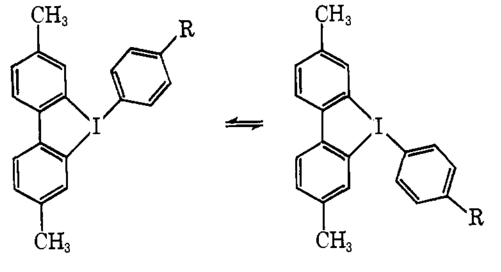
Structure and Stereolability of Triaryliodine(III) Compounds. Degenerate Isomerization of 5-Phenyl-5*H*-dibenziodole

Sir:

We report here the results of nuclear magnetic resonance studies of 5-phenyl- and 5-(*p*-trifluoromethylphenyl)-3,7-dimethyl-5*H*-dibenziodole (**1a** and **1b**) which demonstrate that these triaryliodine compounds have a nonsymmetric planar orientation of iodine–carbon bonds and that the barrier to unimolecular degenerate isomerization is greater than 15 kcal/mol.



1a, R = H
b, R = CF_3

As part of their pioneering studies of high valent organometalloid compounds, Wittig and coworkers[1] reported the synthesis of triphenyliodine by the reaction of diphenyliodonium iodide with phenyllithium. This compound decomposes below −10°, but Clauss[2] subsequently prepared the more stable cyclic analog, 5-phenyl-5*H*-dibenziodole. Studies of the chemistry of these compounds have recently been reported by Beringer and Chang,[3] but little is known of their structure and configurational stability.

Compounds **1a** and **1b** were prepared[2,3a] by the reaction of 3,7-dimethyldibenziodolium iodide[4] with phenyllithium or *p*-trifluoromethylphenyllithium in ether at 0°. The bright yellow solid was twice recrystallized from ether. It is stable at room temperature for several hours and when pure can be stored at −20° for long periods. Solutions are much less stable, but if air and moisture are rigorously excluded they can be kept 1 hr at room temperature with little decomposition.

The nmr spectra of toluene-d_8 solutions of **1a** and **1b** show two singlets in the methyl region (**1a**, δ 1.88, 2.24; **1b**, δ 1.83, 2.21) and a complex aromatic pattern. The observation of nonequivalent methyl signals rules out symmetrical pyramidal or planar structures for **1** and shows that the arrangement of bonds around iodine is similar to that found for $PhICl_2$[5a] which has a planar T-shaped structure,[6] as do other related trisubstituted hypervalent halogen compounds.[5] Solution ^{19}F nmr spectra of BrF_3 give a singlet,[7a,b] but at low temperature[7] and in the gas phase[7c] ClF_3 shows the expected A_2B pattern. An exchange mechanism involving intermolecular fluorine exchange by formation of bridged dimers was suggested for these compounds.

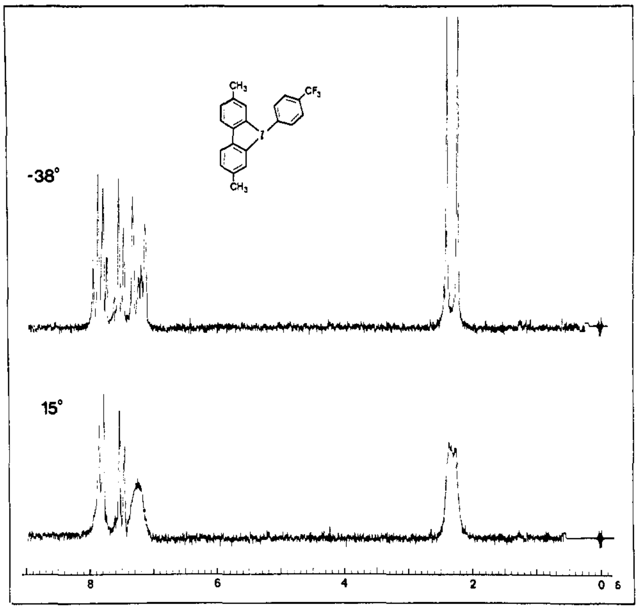


Figure 1. Proton nmr spectra of **1b** in tetrachloroethylene solution at −38 and 15°.

The line shapes of the nmr methyl resonances of **1a** and **1b** show a temperature dependence consistent with a dynamic process which interchanges the environments of the two methyl groups. The coalescence temperatures for solutions in benzene, toluene-d_8, chlorobenzene, tetrachloroethylene, and tetrahydrofuran are between 15 and 60°. Apart from the decomposition, which is quite rapid above 40°,[3a] all line shape changes are reversible.

The low-temperature spectrum of **1b** in tetrachloroethylene (Figure 1, −38°) has methyl singlets at δ 2.24 and 2.41, and an aromatic pattern which can be assigned on the basis of two superimposed 1,2,4-trisubstituted phenyl absorptions. At higher temperatures both the aromatic and methyl peaks broaden (Figure 1, 15°). The simultaneous broadening of the methyl and biphenyl aromatic resonances while the AA′BB′ pattern of the *p*-trifluoromethylphenyl group remains unaffected demonstrates that the temperature dependence is caused by the degenerate isomerization of the aryl substituent between two equivalent sites.

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